

Two Cu(II)-Nitronyl Nitroxide Complexes Including Cyclic Dimer: Synthesis, Structures and Magnetic Interactions

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Abstract

Using two new flexible and functional nitronyl nitroxide radicals as ligands, two copper (II) complexes $\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO}3\text{Py})_2\}_n$ (**1**) and $[\text{Cu}(\text{hfac})_2(\text{NIT}o\text{PhO}3\text{Py})]_2$ (**2**) ($\text{NIT}m\text{PhO}3\text{Py} = 2-[(3\text{-methoxy-pyridinyl})\text{phen-3-yl}]-4,4,5,5\text{-tetramethylimidazoline-1-oxyl-3-oxide}$, $\text{NIT}o\text{PhO}3\text{Py} = 2-[(3\text{-methoxy-pyridinyl})\text{phen-2-yl}]-4,4,5,5\text{-tetramethylimidazoline-1-oxyl-3-oxide}$, $\text{hfac} = \text{hexafluoroacetylacetone}$), have been characterized structurally and magnetically. The X-ray crystal analyses showed that complex **1** displayed a chain polymer structure which formed with $\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO}3\text{Py})_2\}_n$ due to the cross-linking of two cyclic binuclear fragments $\{[\text{Cu}(\text{hfac})_2]_2(\text{NIT}m\text{PhO}3\text{Py})_2\}$ via the bridging unit $[\text{Cu}(\text{hfac})_2]$; complex **2** presented a binuclear cyclic structure $[\text{Cu}(\text{hfac})_2]_2(\text{NIT}o\text{PhO}3\text{Py})_2$. The magnetic behaviors of the two complexes **1** and **2** have been investigated. Magnetic studies showed that antiferromagnetic interactions dominated in complex **1**, while there existed ferromagnetic interactions between Cu(II) and coordinated NO group in complex **2**.

Keywords

Flexible Nitronyl Nitroxide, Cu(II) Complex, Synthesis, Characterization, Magnetic Property

1. Introduction

The coordination complexes of paramagnetic metal ions with organic radical ligands have recently attracted considerable interest on exploiting new molecular-based magnetic materials [1] [2]. Due to exceptional stability and easy of chemical modification as well as diverse coordination modes, nitronyl nitroxide

radicals (NITRs) as building blocks have been thought as an appealing strategy for synthesizing heterospin molecular-based magnetic materials [3] [4] [5]. Up to now, many metal-NITR compounds have been reported, which provided more information about structural-magnetic correlation [6]-[11]. As well known, modest changes in the structure of radical ligands or in the coordination sphere of such complexes can sometimes result in large changes in electronic and magnetic behavior. Metal-radical complexes with definite geometry are good candidates for fundamental studies of magnetostructural correlations, especially, how the structural factors affect the metal-radical interactions. Such investigation is necessary not only for understanding the magnetic exchange mechanism between the metal ion and the radical ligand but also for the developing of novel molecular magnetic materials. Among these metal-NITR complexes, copper (II) compounds are often used as unique objects for investigating the novel structures and the peculiarities of magnetic exchange pathways, for instance, Cu(II)-NITR complexes with different R groups can form mononuclear and polynuclear complexes, as well as one-dimensional and higher dimensional architectures, which result in different magnetic interactions between Cu(II) and NITR radicals [12] [13]. Investigations reveal that if ONCNO of the nitronyl nitroxide group links with Cu(II) ion at axial position, the magnetic property tends to be a ferromagnetic interaction, whereas equatorial coordinates to Cu(II) ion generally prefers to an antiferromagnetic interaction [14] [15] [16]. To obtain novel structural complexes and gain more information on magnetic interactions between transition metal ions and NITR radical ligands, we concentrate our study on designing and synthesizing new functional radical ligand and M-NITR compounds. For ease of comparison, we have designed and prepared two flexible and isomeric nitronyl nitroxide ligand, 2-[(3-methoxy-pyridinyl) phen-3-yl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT*m*PhO3Py) and 2-[(3-methoxy-pyridinyl) phen-2-yl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT*o*-PhO3Py). Using the two radical as ligands, we successfully obtain two new complexes $\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO3Py})_2\}_n$ (**1**) and $[\text{Cu}(\text{hfac})_2(\text{NIT}o\text{PhO3Py})_2]_2$ (**2**). In this paper, we report the syntheses, crystal structures, and magnetic properties of the two compounds. X-ray crystal structure analyses show that complex **1** displays a chain polymer $\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO3Py})_2\}_n$ due to $\{[\text{Cu}(\text{hfac})_2]_2(\text{NIT}m\text{PhO3Py})_2\}$ binuclear fragments via one $[\text{Cu}(\text{hfac})_2]$ bridging unit; complex **2** is a binuclear cyclic structure. Magnetic studies show that antiferromagnetic interactions dominate in complex **1**. For complex **2**, the ferromagnetic interactions exist between Cu(II) and coordinated NO group, which origins from the orthogonal arrangement of the Cu(II) magnetic orbital and nitronyl nitroxide magnetic orbitals (π^*).

2. Experimental

2.1. General Procedure

All reagents were purchased from commercial sources and were used without further purification. Nitronyl nitroxide radical ligands have been prepared ac-

according to literature methods [17] [18] [19]. All reactions were conducted in aerobic conditions. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. Infrared spectra were taken on a Bruker Tensor 27 Fourier transformed infrared (FTIR) spectroscopy in the region 4000 - 400 cm^{-1} , using KBr pellets. Ultraviolet-visible spectra (UV-Vis) were recorded on a Cary 50 UV-Vis spectrometer in alcohol. Magnetic data were recorded by a Quantum Design MPMS XL-7 SQUID in the temperature range of 2 - 300 K at a magnetic field strength of 1000 Oe. The corrections of diamagnetic contributions of magnetic data were carried out for the constituent atoms estimated from Pascal's constants.

2.2. Synthesis

2.2.1. Synthesis of Complex 1 $\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO}3\text{Py})_2\}_n$

$\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ (0.01016 g, 0.02 mmol) was dissolved in boiling *n*-heptane (15 mL). After stirring for 2.5 h, the solution was cooled to 70 °C and $\text{NIT}m\text{PhO}3\text{Py}$ (0.0069 g, 0.02 mmol) in CH_2Cl_2 (5 mL) was added with refluxing for 30 min. Then, the solution was cooled to the room temperature, filtered and the filtrate was stored in a refrigerator. After several weeks, dark-blue block crystals suitable for X-ray analysis were collected. Yield: 36%. Anal. Calcd. For $\text{C}_{68}\text{H}_{50}\text{Cu}_3\text{F}_{36}\text{N}_6\text{O}_{18}$ (%): C, 38.64; H, 2.38; N, 3.98. Found: C, 38.76; H, 2.42; N, 3.92. FTIR (KBr, cm^{-1}): 1646 (s), 1526 (m), 1465 (s), 1364 (m), 1250 (s), 1191 (s), 1139 (s), 792 (s), 668 (s), 587 (s). UV-Vis: 303 nm, 357 nm, 567 nm.

2.2.2. Synthesis of Complex 2 $[\text{Cu}(\text{hfac})_2]_2(\text{NIT}o\text{PhO}3\text{Py})_2$

Complex 2 was synthesized using the same procedure for 1 with $\text{NIT}o\text{PhO}3\text{Py}$ instead of $\text{NIT}m\text{PhO}3\text{Py}$. After a few days, blue block crystals were collected. Yield: 44%. Anal. Calcd. for $\text{C}_{58}\text{H}_{48}\text{Cu}_2\text{F}_{24}\text{N}_6\text{O}_{14}$ (%): C, 42.58; H, 2.96; N, 5.14. Found: C, 42.71; H, 3.02; N, 5.16. FTIR (KBr, cm^{-1}): 1646 (s), 1526 (m), 1363 (m), 1254 (s), 1193 (s), 1138 (s), 750 (s), 667 (s), 588 (s). UV-Vis: 305 nm, 353 nm, 552 nm.

2.3. X-Ray Crystallographic Study

Single crystal X-ray diffraction data of 1 and 2 were collected at 293 K on Bruker Smart Apex II CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods with SHELXS-2018 program [20] and refined by full-matrix least-squares on F^2 using SHELXTL-2018 [21]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Crystallographic data as well as bond distances and angles are presented in Table 1 and Table 2.

3. Results and Discussion

3.1. Crystal Structures

As shown, both of radical ligands, $\text{NIT}m\text{PhO}3\text{Py}$ and $\text{NIT}o\text{PhO}3\text{Py}$, are the

Table 1. Crystallographic data and processing parameters for **1** and **2**.

Complex	$\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO}3\text{Py})_2\}_n$ 1	$[\text{Cu}(\text{hfac})_2]_2(\text{NIT}o\text{PhO}3\text{Py})_2$ 2
Empirical formula	$\text{C}_{68}\text{H}_{50}\text{Cu}_3\text{F}_{36}\text{N}_6\text{O}_{18}$	$\text{C}_{58}\text{H}_{48}\text{Cu}_2\text{F}_{24}\text{N}_6\text{O}_{14}$
Formula weight	2113.76	1636.10
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P - 1$
<i>a</i> (Å)	19.9811 (9)	10.358 (2)
<i>b</i> (Å)	18.2374 (8)	10.521 (2)
<i>c</i> (Å)	24.3643 (12)	17.486 (4)
α (°)	90.00	79.50 (3)
β (°)	100.922 (2)	87.62 (3)
γ (°)	90.00	63.58 (3)
Volume (Å ³)	8717.6 (7)	1676.4 (6)
Z	4	1
Calculated density ($\text{mg}\cdot\text{m}^{-3}$)	1.611	1.621
Absorption coefficient (mm^{-1})	0.868	0.767
F(000)	4220	824
Crystal size (mm^3)	$0.10 \times 0.10 \times 0.10$	$0.10 \times 0.10 \times 0.10$
θ range for data collection (°)	2.64 to 22.06	2.20 to 25.39
Reflections Collected/unique	54,971/8530 [R(int) = 0.0824]	19,030/5904 [R(int) = 0.0585]
Data/restraints/ parameters	8530/0/1180	5904/13/469
Goodness-of-fit on F^2	1.051	1.135
R_I [$I > 2\sigma(I)$]	0.0807	0.0806
wR_2 [$I > 2\sigma(I)$]	0.2232	0.2268
R_I (all data)	0.1360	0.0975
wR_2 (all data)	0.2587	0.2445

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

$\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO}3\text{Py})_2\}_n$ 1			
Bond lengths (Å)		Bond angles (°)	
Cu1-O6	1.967 (4)	O6-Cu1-O5	90.11

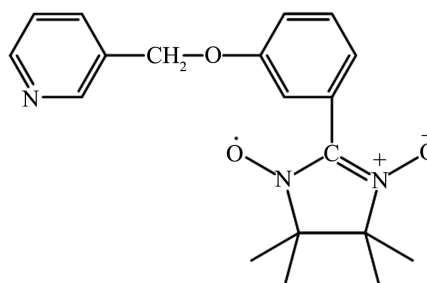
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Cu1-O5	1.974 (4)	O6-Cu1-O7	84.98
Cu1-O7	1.973 (4)	O5-Cu1-O7	174.99
Cu1-N5	2.004 (4)	N5-Cu1-O1	93.67
Cu1-O8	2.286 (5)	O6-Cu1-O8	83.84
Cu1-O1	2.406 (5)	O5-Cu1-O8	94.05
Cu2-O10	1.959 (4)	N5-Cu1-O8	91.72
Cu2-O9	1.963 (4)	O1-Cu1-O8	174.16
Cu2-O11	1.965 (4)	O4-Cu2-O12	174.68
Cu2-N6	1.991 (5)	O10-Cu2-O9	89.72
Cu2-O12	2.264 (5)	O10-Cu2-O11	86.21
Cu2-O4	2.517 (1)	O9-Cu2-O11	174.56
Cu3-O2	2.516 (7)	O9-Cu2-N6	91.53
Cu3-O14	1.924 (4)	O14-Cu3-O15	86.21
Cu3-O15	1.935 (4)	O14-Cu3-O13	92.62
Cu3-O13	1.935 (5)	O15-Cu3-O13	161.10
Cu3-O16	1.952 (5)	O13-Cu3-O16	94.60
Cu3-O3	2.464 (5)	O2-Cu3-O3	170.17
N1-O1	1.280 (6)	N1-O1-Cu1	122.07
N2-O2	1.265 (6)	N4-O4-Cu2	118.02
N3-O3	1.258 (6)	N3-O3-Cu3	131.06
N4-O4	1.279 (6)	N2-O2-Cu3	132.32

[Cu(hfac)₂]₂(NIToPhO3Py)₂ **2**

Bond lengths (Å)		Bond angles (°)	
Cu1-O4	1.944 (4)	O4-Cu1-O7	171.80
Cu1-O7	1.955 (4)	O4-Cu1-O5	89.30
Cu1-O5	1.974 (4)	O7-Cu1-O5	86.29
Cu1-N1	2.018 (4)	O4-Cu1-N1	90.09
Cu1-O6	2.297 (5)	O7-Cu1-N1	93.67
Cu1-O2	2.666 (3)	O4-Cu1-O6	101.21
N2-O2	1.281 (6)	O7-Cu1-O6	85.43
O3-N3	1.277 (6)	O5-Cu1-O6	86.52
N2-C13	1.327 (7)	O2-Cu1-O6	177.02
N2-C14	1.513 (7)	O2-Cu1-O5	91.20
N3-C13	1.338 (7)	O2-Cu1-O4	81.23
N3-C15	1.501 (9)	O2-Cu1-N1	82.97

bridging tridentate ligand (see **Scheme 1** and **Scheme 2**), so it links metal ions by “head and head” through two N-O groups or “head and tail” using N-O unit and N-pyridine from two different nitronyl nitroxide ligands. Single-crystal X-ray diffraction analysis indicates complex **1** crystallizes in the monoclinic space group $P2_1/c$. In each unit cell, there are three unsymmetrical Cu(II) atoms; each Cu(II) ion is coordinated by O-atom/N-atom of NITR radicals and O-atom of hfac ligands in distorted octahedron geometry. The molecular structure of complex **1** is shown in **Figure 1(a)** and **Figure 1(b)**.



Scheme 1. The structure of NITmPhO3Py.

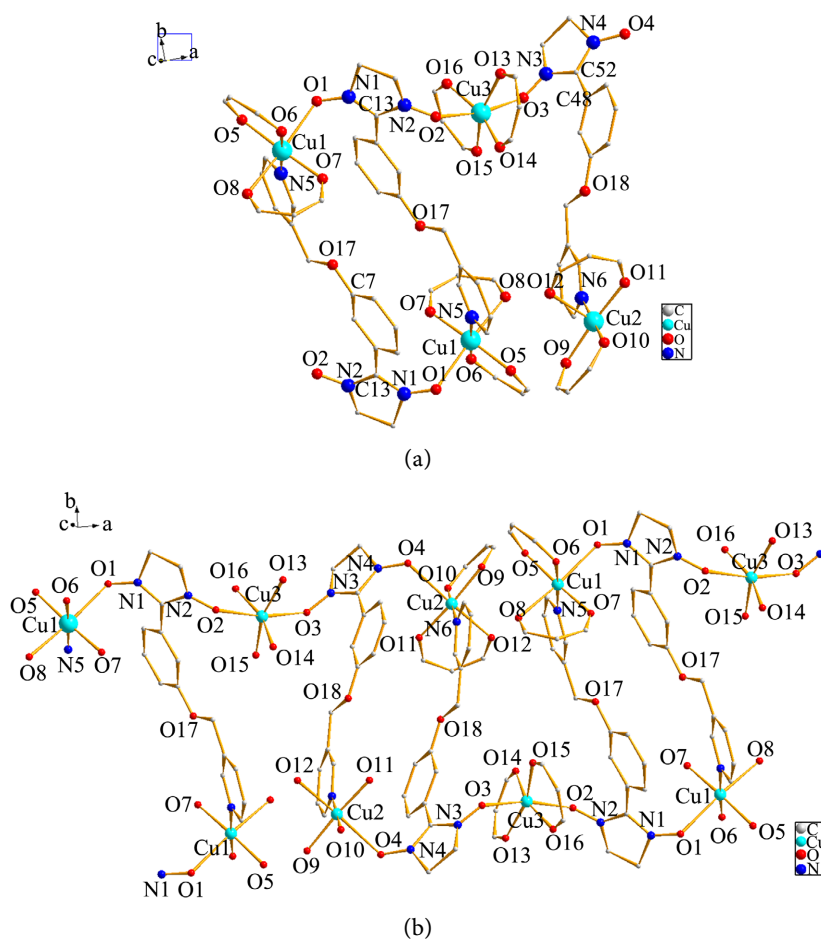
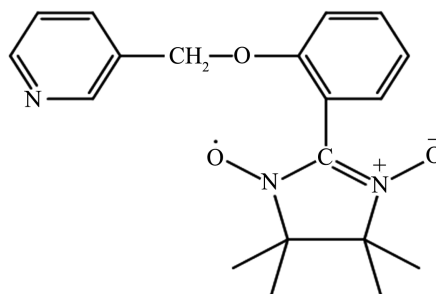


Figure 1. (upper) Simplified crystal structure of **1**. CF_3 , CH_3 and hydrogens are omitted for clarity; (down) Viewing of the 1D packing structure of **1**.



Scheme 2. The structure of NIT*o*PhO3Py.

In complex **1**, there are two different cyclic dimers [(Cu1-Radical)₂] and [(Cu2-Radical)₂], which constructed from two NIT*m*PhO3Py ligands and two Cu(hfac)₂ units, forming a rectangle-like centrosymmetric dimer structure. In each cyclic dimer [Cu(hfac)-Radical]₂, two NIT*m*PhO3Py radicals as bridging ligands link two Cu(hfac)₂ units through the oxygen atom of ONCNO group and pyridine nitrogen atom using ‘head and tail’ mode. For different cyclic dimer, Cu(II) ion displays an elongated octahedral geometry. To each Cu(II) ion, there are six coordination sites which are occupied by four oxygen atoms from hfac ligand, one oxygen atom from the nitronyl nitroxide unit and one nitrogen atom from the pyridine ring. The oxygen atoms from the radical and the nitrogen atom from another radical are coordinated to Cu(II) in a *cis*-configuration. The O-atom of ONCNO group occupied axial coordinate site in the adduct of Cu(hfac)₂. The apical Cu (Cu1 and Cu2)-O (radical) and Cu (Cu1 and Cu2)-O (hfac) bond lengths are 2.406 (5) - 2.517 (1) Å and 2.286 (5) - 2.264 (5) Å, respectively. The bonds Cu-O (hfac) and Cu-N (pyridine) in the equatorial position are shorter than that Cu-O bonds in the apical one, which dues to the Jahn-Teller elongation effect. Cu (Cu1 and Cu2)-O (radical) are larger than the reported [22]. Similar to Cu1, Cu2 links to Cu3 by two NIT*m*PhO3Py radicals through “head and head” mode. Two cyclic dimers bind to the Cu3 unit through two NO groups, which results in a chain structure (**Figure 1(b)**). On the radical ligands, the O-N-C-N-O is almost coplanar. The bond angles are differences (N1-O1-Cu1 122.07°, N4-O4-Cu2 118.02°, N2-O2-Cu3 132.32° and N3-O3-Cu3 131.06), which are the important factors to affect the magnetic interaction.

X-ray diffraction analysis indicates that complex **2** is in triclinic *P*₁ space group, which is a cyclic dimer composed of two Cu(II) ions and two NIT*o*-PhO3Py radicals. Two NIT*o*PhO3Py radical act as bridging ligand bonding with two Cu(hfac)₂ to generate a four-spin cyclic dimer. On the NIT*o*PhO3Py ligand, the imidazole (ONCNO) is coplanar, but has a dihedral angle of 56.3° with the phenyl ring. Each Cu(II) ion adopts a distorted octahedral (**Figure 2**). It consists of four oxygen atoms from two hfac units, one nitrogen atom from one NIT*o*-PhO3Py radical ligand and one oxygen atom from another radical ligand. The Cu-N bond distance of 2.018 Å is shorter than the corresponding Cu-O (nitronyl nitroxide groups) bond length, which are comparable to those observed in the previously reported cyclic metal-nitroxide dimers [23] [24]. The bonding

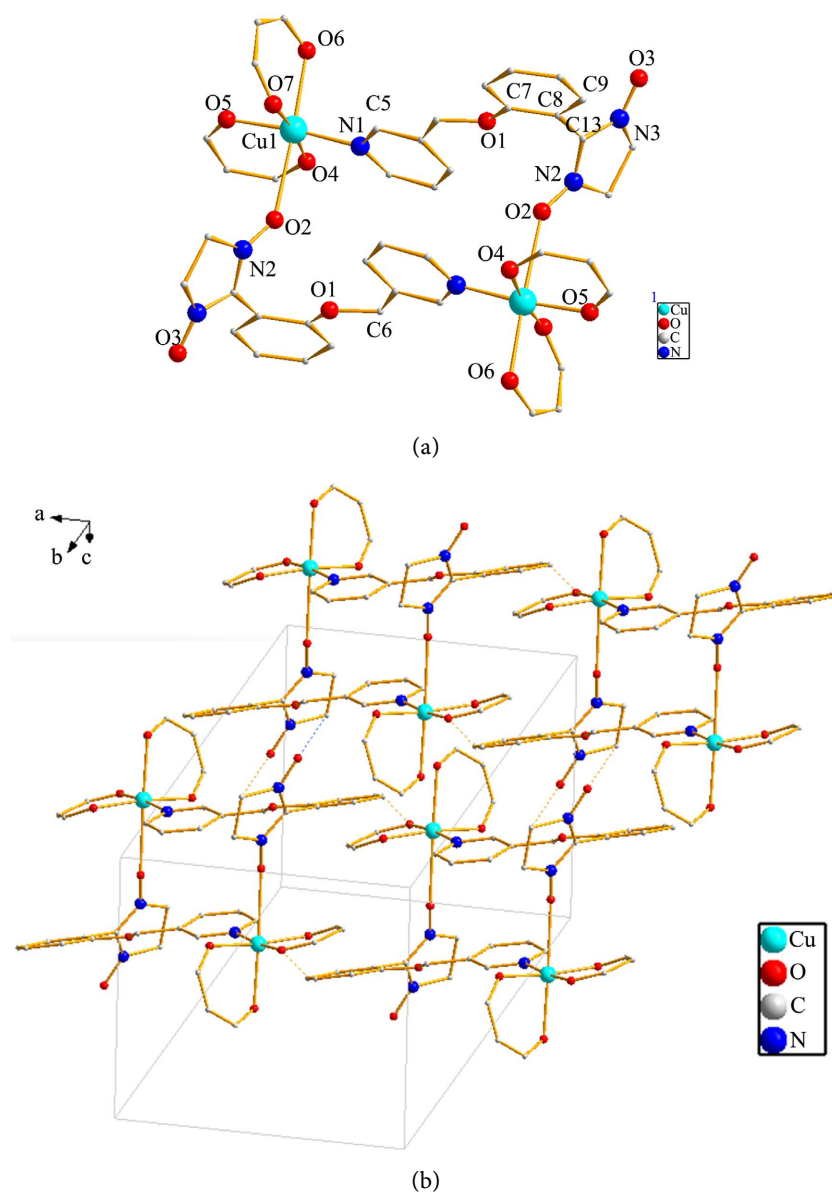


Figure 2. (upper) The molecular structure of **2**. CF₃, CH₃ and hydrogen are omitted for clarity; (down) Viewing of the 3D packing structure of **2**.

angle of N2-O2-Cu1 is 146.61°. The dihedral angle between ONCNO and N2-O2-Cu1 is 50.28°, which is smaller than those in complex **1** (73.65° - 74.1°). The intradimeric Cu...Cu distance of 10.358 Å is longer than the shortest interdimeric Cu...Cu distance of 9.141 Å. In the crystal lattice (**Figure 2(b)**), the cyclic dimers are arranged parallel along the c-axis.

3.2. Magnetic Properties

For the complexes **1** and **2**, the magnetic susceptibility was investigated in the temperature range 2 - 300 K under a magnetic field of 1000 Oe. Data were corrected by the magnetization of the sample holder and diamagnetic contributions, which were estimated from Pascal's constants. The temperature-dependent

magnetic susceptibility of complex **1** and **2** are displayed in **Figure 3** and **Figure 4**.

As shown in **Figure 3(a)** and **Figure 3(b)**, for complex **1**, the room temperature $\chi_M T$ value is $1.286 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, lower than the expected values ($1.875 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$) for uncoupled three Cu(II) ion plus two radicals ($S = 1/2$) with $g = 2.0$, indicating the existence of antiferromagnetic interactions. With the decrease of temperature, the $\chi_M T$ value decrease from $1.286 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K down to $0.972 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at about 28 K. After that, the $\chi_M T$ value increases up to $1.014 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K. The variation of $1/\chi_M$ value versus temperature followed the Curie-Weiss equation with the corresponding Curie constant (C) and Weiss constant (θ) of $3.125 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and -8.72 K , respectively, which indicate that the antiferromagnetic interaction between Cu(II) ion and NIT m PhO3Py radical.

The plots of χ_M and $\chi_M T$ versus T for **2** are shown in **Figure 4**.

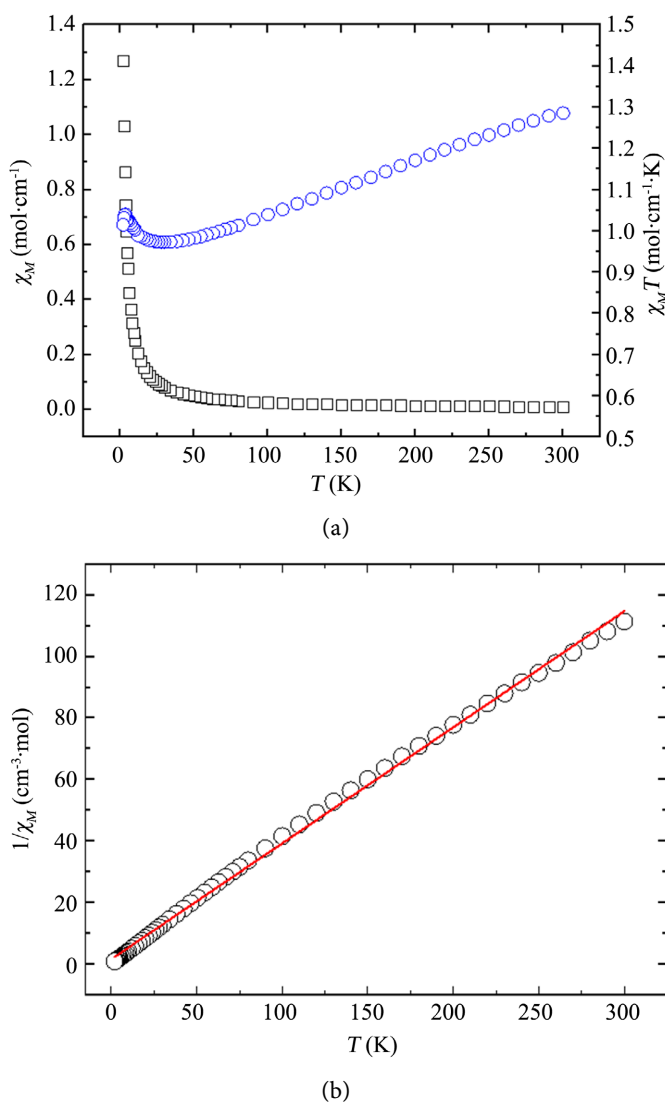


Figure 3. (upper) Temperature dependence of χ_M (\square) and $\chi_M T$ (\circ) vs T of **1**; (down) χ_M^{-1} vs. T (\square) plots obtained for **1**. The solid lines represent the best theoretical fitting.

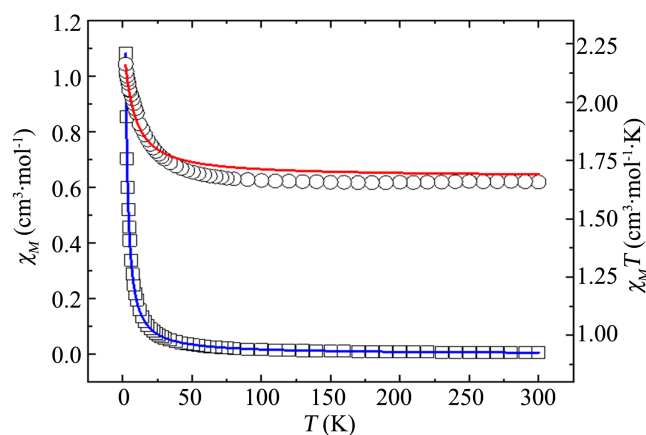


Figure 4. Plots of χ_M (\square) and $\chi_M T$ (\circ) vs T of complex 2. The solid lines represent the best theoretical fitting.

For complex 2, the $\chi_M T$ value at 300 K is $1.65 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is higher than the value expected for two uncoupled Cu(II) ions ($S = 1/2$) and two nitroxide ligands ($S = 1/2$) ($1.50 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, assuming $g = 2.0$). The value of $\chi_M T$ gradually increases upon cooling, indicating the existence of ferromagnetic exchange in the cyclic dimer. The magnetic susceptibility was analyzed with the Hamiltonian for a rectangular four-spin ($S = 1/2$) system [24].

$$H = g\beta S - 2 \left[J_1 (S_{Cu1} S_{NIT1} + S_{Cu2} S_{NIT2}) + J_2 (S_{Cu1} S_{NIT2} + S_{Cu2} S_{NIT1}) \right]$$

N , k and β constants in Equation (1) have their usual meanings. The exchange parameter J_1 reflects the magnetic coupling between the Cu(II) ion and the directly bonded nitroxide unit. The parameter J_2 reflects the magnetic exchange of the Cu(II) ion and pyridine rings. The expression of magnetic susceptibility, derived from the Hamiltonian, is given as Equation (1).

$$\chi_M = \frac{2N}{kT} g^2 \beta^2 \left[\frac{5 \exp(Q/kT) + R}{5 \exp(Q/kT) + 3R + \exp((S-Q)/kT) + \exp(-(S+Q)/kT)} \right] \quad (1)$$

where

$$Q = J_1 + J_2$$

$$R = \exp((J_1 - J_2)/kT) + \exp((J_2 - J_1)/kT) + \exp(-(J_1 - J_2)/kT)$$

$$S = 2(J_1^2 + J_2^2 - J_1 J_2)^{1/2}$$

The best fitting gives $g = 2.01$, $J_1 = 4.36 \text{ cm}^{-1}$ and $J_2 = 0.10 \text{ cm}^{-1}$ with the agreement factor $R = 1.24 \times 10^{-6}$. As the analysis of structure indicates, the oxygen atom of the NOCNO group locates in the axial position of the Cu(II) coordination geometry. In such a way, the magnetic orbitals of the Cu(II) ion ($d_{x^2-y^2}$) and the ONCNO group (π^*) are orthogonal. The coupling between the Cu(II) ion and the NO group of radical should be ferromagnetic interaction [25] [26]. The small value of J_2 suggests the interaction between the Cu(II) ion and the pyridine unit of radical ligands is very weak, which is consistent with the spin pola-

rization role [14] [15] [16].

4. Conclusion

In order to ease comparing and investigating the magnetostructural correlations, we designed and synthesized two flexible and isomeric nitronyl nitroxide radicals. Using the nitronyl nitroxide radicals as ligands, two new complexes $\{[\text{Cu}(\text{hfac})_2]_3(\text{NIT}m\text{PhO}3\text{Py})_2\}_n$ **1** and $[\text{Cu}(\text{hfac})_2]_2(\text{NIT}o\text{PhO}3\text{Py})_2$ **2** were synthesized and characterized structurally. X-ray crystal structure analyses show, in complex **1**, that two cyclic dimers were linked by $\text{Cu}(\text{hfac})_2$ molecule forming 1D chains. For complex **2**, it is a binuclear cyclic structure. For complex **1**, there is an antiferromagnetic coupling between the Cu(II) ion and the directly bonding nitroxide group. Complex **2** exhibits a ferromagnetic exchange between the Cu(II) ion and ONCNO unit due to the axial elongated Cu-ON bond and a very weak exchange of Cu(II)-nitroxide through the pyridine rings.

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Conflicts of Interest

No potential conflict of interest was reported by the authors.

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC reference numbers 2157142 and 2157124.

The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.